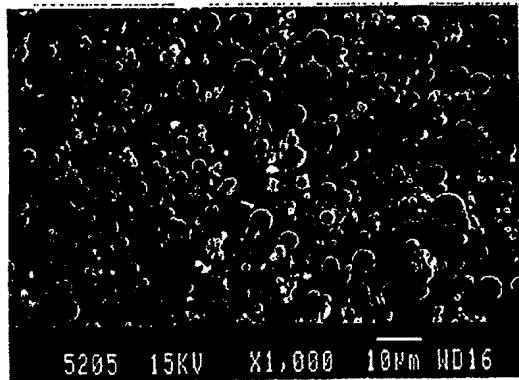


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(54) Title: PROCESSED FLY ASH AS A FILLER IN PLASTICS



Particle shape of fine clean AEP ash

## (57) Abstract

Fly ash generated from low NO<sub>X</sub> burners at American Electric Power's Glen Lyn facility was beneficiated to remove residual carbon, magnetic particles, and cenospheres. The clean fly ash has a mean particle size of about 30 microns. The clean fly ash is classified to separate the clean fly ash into its coarse and fine fractions. The resulting fine fraction has a mean particle size of less than about 10 microns. The clean fine ash is coated with a silane coupling agent and added to polypropylene, low density polyethylene, and high density polyethylene at various levels. These mixtures are in turn used to make articles by injection molding.

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### Processed Fly Ash as a Filler in Plastics

#### **FIELD OF THE INVENTION**

5 This invention relates to a process for treating fly ash and for utilizing the treated fly ash as a filler.

#### **BACKGROUND OF THE INVENTION**

10 The United States alone generates millions of tons of fly ash per year from coal fired electrical power plants and the like. Landfill disposal of fly ash can be costly. One alternative to disposal includes recycling the fly ash for use as a filler in applications such as roadways or concrete pavements.

15 The carbon content of fly ash has increased, in part, due to the 1990 Clean Air Act Amendments which forced many utilities to retrofit with low NO<sub>x</sub> burners to meet the new standards. This prohibits its use in cement and concrete products and its potential 20 penetration into a number of other markets.

It would be desirable to expand the applications in which fly ash may be utilized as a filler.

#### **SUMMARY OF THE INVENTION**

25 Fly ash is not typically utilized as filler in applications requiring higher grade filler, primarily due to inconsistencies in fly ash quality, such as large variations in particle size and undesirable contaminants, which could impair the characteristics of 30 a final product. It has been found that fly ash treated according to the method of one embodiment of this invention is useful as filler in applications, such as plastic products. Further, it has been found that such fly ash filled products retain performance 35 characteristics similar to conventional commercial fillers.

One embodiment of the present invention is a process for producing a filler from a fly ash material by cleaning and separating the finest fraction. The

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process generally comprises the steps of cleaning the fly ash material to remove at least a portion of the carbon content, cenospheres or magnetic particles, and subjecting the fly ash material to size classification to obtain a fines fraction having a mean particle size less than about 30 microns. Additional steps of calcining and coating coupling agent also can be used to improve fly ash filler quality. The resulting fly ash particles are ultra fine compared to typical fly ash particles. For example, fly ash particles on the order of about 2 to about 7 microns are achievable. The particle size distribution of the resulting fly ash is narrower than that of two comparable commercial fillers (see Tables 2 and 7). In addition, the unique spherical shape can be an advantage over most existing commercial fillers.

Another embodiment of the present invention is a process for the manufacture of a plastic article. This process comprises the steps of cleaning a fly ash material to remove at least a portion of the carbon content, cenospheres or magnetic particles; subjecting the fly ash material to size classification to obtain a fines fraction having a mean particle size less than about 30 microns; and compounding the resulting clean fines fraction with a plastic matrix. Calcining and coating fly ash with a coupling agent also can be carried out before compounding. Preferably, this embodiment comprises the steps of: cleaning a fly ash material so the carbon content is less than about 6%; size classifying the fly ash material to obtain a fines fraction having a mean particle size less than about 30 microns; mixing the clean fines fraction with a plastic matrix such as polyethylene or polypropylene to form a mixture; and heating the mixture to form a compound. The resulting compound may be molded, for example, by injection molding, extrusion molding or compression molding to form the desired plastic article. The polymers with ash filler can be used to produce

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commercial automotive parts without impairing injection moldability, dimension accuracy and surface quality in comparison with the commercially filled polymer compounds.

5 Another embodiment of the present invention is a process for producing a filler from a fly ash material by cleaning and grinding the fly ash. The process generally comprises the steps of cleaning the fly ash material to remove at least a portion of the carbon  
10 content, cenospheres or magnetic particles, and subjecting the fly ash material to a mill to reduce the fly ash size to less than about 30 microns.

15 A further embodiment of the present invention is a plastic article comprising a plastic matrix having a fly ash filler dispersed throughout, wherein the fly ash filler has a mean particle size of less than about 30 microns. The plastic article is preferably an automobile part manufactured by the process of the invention.

20

#### DESCRIPTION OF THE DRAWINGS

Figure 1 shows a particle shape of fine clean AEP ash.

25

Figure 2 shows a particle shape of commercial alumino-silicate filler.

Figure 3 shows fracture surface of polypropylene with 40 phr fine clean AEP ash.

Figure 4 shows fracture surface of polypropylene with 40 phr  $\text{CaCO}_3$  filler.

30

Figure 5 shows fracture surface of low density polyethylene with 40 phr fine clean AEP ash.

Figure 6 shows fracture surface of low density polyethylene with 40 phr  $\text{CaCO}_3$  filler.

35

Figure 7 shows fracture surface of high density polyethylene with 40 phr fine clean AEP ash.

Figure 8 shows fracture surface of high density polyethylene with 40 phr  $\text{CaCO}_3$  filler.

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Figure 9 shows trim clips produced from an ash filled polymer.

Figure 10 shows wiring harness supports produced from an ash filled polymer.

5

#### DETAILED DESCRIPTION OF THE INVENTION

##### BENEFICIATION

In accordance with the first step of the method of the present invention, the fly ash material is cleaned to remove at least a portion of the carbon content, 10 cenospheres or magnetic particles. Carbon removal may be achieved by various methods customary in the art, such as by froth flotation; by heating the fly ash to burn off the carbon, for example, at about 600°C or 15 higher for at least about 1 to 2 hours; by gravitational separation; or by triboelectric or electrostatic separation. Froth flotation is preferred and generally entails adding a frothing agent to a fly ash slurry and imposing an air stream into the solution 20 thereby producing a frothing layer containing hydrophobic unburned carbon particles, which may be removed. Preferably, the residual carbon content is less than 6%; more preferably, less than 3%; most preferably, less than about 1%.

25 Carbon content may be determined, for example, by loss on ignition (LOI). To make a LOI measurement, the fly ash is weighed, then the carbon is burned off at temperatures of about 600°C or more, and the weight change after burning off the carbon is noted.

30 In addition to reducing the carbon content, further ash beneficiation may be performed to remove the magnetic particles and cenospheres from fly ash. Generally, a more complete beneficiation process may include the steps of forming a slurry mixture of a fly ash material and a liquid, such as water; gravitationally separating cenospheres from the slurry; separating a magnetic fraction from the slurry by 35 subjecting the slurry to a magnetic field; and

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separating the unburned carbon from the slurry by froth flotation. A more detailed description of such a beneficiation process can be found, for example in U.S. Patents No. 5,047,145 and 5,227,047 which are herein 5 fully incorporated by reference. Depending on the quality of fly ash required in the final application, some steps in the beneficiation process may be omitted. Preferably, at least the carbon reduction step is included.

10 This cleaning step may be performed before or after the size classification step described below. If performed before and if an air classifier is utilized, then the clean fly ash should be dried to remove liquids prior to the air classification step.

15 Optionally, if trace contamination material remains on the fly ash surface after beneficiation, such as flotation reagent, then the fly ash can be calcined before or after size classification at a temperature higher than about 200°C, preferably higher than about 20 500°C but lower than about 1000°C, to evaporate or burn off the contamination material, resulting in very clean fly ash.

#### SIZE SELECTION

25 The second step of the method of the present invention is a size selection of the fly ash material to obtain a fines fraction having a mean particle size less than about 10 microns. Size selection may be achieved by size classification which may be carried 30 out, for example, by air classification or by wet classification.

In general, when air classifying particles, the coarser particles traverse to or remain at the rotor periphery where they may be drawn out and collected; 35 typically, the fines may be drawn out from a center outlet of the classifier chamber. Increased air flow increases the particle size cut point and thus increases the coarseness and yield of the fines

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fraction. In contrast, increasing the rotor speed, increases the fineness of the fine product and decreases its yield. Preferably, the rotor speed is between about 1000 and to about 2000 rotations per 5 minute (RPM).

Wet classification may be carried out with a hydrocyclone or a sedimentation tank. Typically, increasing the operating pressure of a hydrocyclone provides higher throughput and a sharper cut at a finer 10 cut point.

After size classification, the resulting fines fraction preferably has a mean particle size less than about 20 microns; more preferably, less than about 10 microns. A fines fraction may be obtained having a 15 mean particle size of less than about 6 microns, or less than about 3 microns.

To determine the optimum conditions for the "cut" or mean particle size desired, several air classification tests were run under different operating 20 parameters. After each test, the particle size distributions and yields of the resulting coarse and fine fractions were established using a Leeds & Northrup Microtrac analyzer (see Table 1). The parameters of Test #10 (55 standard cubic feet per 25 minute, 1000 RPM) offered the most favorable results and these parameters were used to produce more than 3 kilograms of clean ash with a mean particle size of less than 5 microns as described in Example 1.

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Table 1  
Air Classification Results

5	Test No.	Flow Rate SCFM	RPM	Coarse Fraction		Fine Fraction	
				Mean Size Microns	Yield %	Mean Size Microns	Yield %
	4	45	1800	28.11	95.4	3.46	4.6
	5	55	1800	35.12	94.6	2.95	5.4
10	6	65	1800	33.10	92.2	3.13	7.8
	7	45	1000	39.59	86.1	4.25	13.9
	8	45	2000	36.20	97.9	2.61	2.1
	9	45	3000	29.04	99.3	2.71	0.7
	10	55	1000	38.27	83.3	4.13	16.7
15	11	65	1000	37.69	82.3	4.65	17.7
	12	-	1000	37.33	88.9	21.18	11.1

As an alternative to size classification, the desired mean particle size may be achieved by grinding the fly ash material, for example, in a ball mill.

#### FLY ASH UTILIZATION

The resulting fines fraction of the clean, classified fly ash is useful as filler in articles such as plastics or paints or other coatings. The fly ash may be mixed with the desired matrix material. Preferably, the clean fines fraction is compounded with a plastic matrix. In general, the compounding step includes mixing the clean fines fraction with the plastic matrix while heating the mixture.

The plastic matrix may include any plastic or elastomeric material, such as thermosetting plastics, thermoplastics, advanced thermoplastics and automotive

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elastomers. Representative thermosetting plastics include alkyd, diallyl phthalates, epoxies, melamines, phenolics, polybutadienes, polyesters, silicones, and ureas. Representative thermoplastics include 5 acrylonitrile-butadiene-styrene, acetals, acrylics, aramids, cellulosics, ionomers, low-permeability thermoplastics, nylons, parylenes, polyaryl ether, polyaryl sulfone, polycarbonates, polyesters, polyethersulfone, polyethylenes, polypropylenes, 10 polyallomers, polyimides polyamide-imides, polymethyl pentene, polyphenylene oxides, polyphenylene sulfides, polystyrenes, polysulfones, and vinyls. Representative advanced thermoplastics include polyphenylene sulfide, polysulfone, polyetheretherketone, polyethersulfone, 15 polyetherimide, polyadamide-imide, polyetherketone, polyamide, polyimide, polyarylene sulfide, polyarylene ketone, and polyetherketoneketone. Representative automotive elastomers include butyl, bromobutyl, chlorobutyl, chlorinated polyethylene, chlorosulfonated 20 polyethylene, epichlorohydrin, ethylene-acrylic copolymer, ethylene-propylenediene terpolymer, ethylene-vinyl acetate, fluoroelastomer, fluorosilicone, natural rubber, nitrile, polyacrylate, polychloroprene, styrene-butadiene copolymer, and 25 silicone. Preferably, the plastic matrix includes polypropylene, low density polyethylene, high density polyethylene, vinyls such as, polyvinyl chloride (PVC), polystyrenes, polyacrylics, polycarbonate, acrylonitrile-butadiene-styrene (ABS), thermoplastic 30 polyester (PET), nylon, phenolic resins, polymethyl methacrylate (PMMA), polyamides, polyester, polyurethane, or thermoplastic polyolefin (TPO); more preferably, polypropylene, polyethylene, PVC, polycarbonate, ABS, or nylon. Most preferably, 35 polypropylene or polyethylene.

The plastic matrix may be in various physical forms during mixing with the clean fines fraction. For example, the plastic matrix may be in a solid pellet

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form, a powder form, a liquid form, or a semi-liquid form during mixing with the clean fines fraction.

Preferably, the plastic matrix is in a powder form.

5 The ratio of filler to matrix material may be varied depending on the desired characteristics of the final product. The filler concentration should not be so high that the melted polymer is too viscous to process. Preferably, the concentration of clean fines fraction is less than about 500 parts per hundred parts of plastic matrix (phr) by weight; more preferably less than about 400 phr; most preferably less than about 200 phr. Preferably, the concentration is greater than about 10 phr, more preferably, greater than about 20 phr.

15 A coupling agent may be coated on the filler surface prior to mixing with the matrix to improve bonding between the filler surface and the matrix of polymer. One of the most commonly used coupling agents is Silane which is a series of products

20 formulated for different filler and polymer systems. Dow Corning Z-6032 is suitable for fly ash and compatible with the three polymer systems tested in Example 4. Typical Properties of Dow Corning Z-6032 Silane are as follows: Vinylbenzyl-amine-methoxy functionality; 40% solids; methanol solvent; 0.900 specific gravity at 25C; closed cup flash point of 13 C; 2 centistokes (cS) viscosity at 25 C; suitable diluents include alcohols and water; and a shelf life of approximately 6 months from the date of shipment.

25 Other coupling agents compatible with the polymer of interest may be suitable.

30 The resulting polymer/flyash compounds may be used to produce, for example, automobile parts. Plastic parts filled with fly ash may be produced by any manner customary for producing plastic parts. Injection molding is one of the primary forming processes used by the plastic industry to produce various products. The addition of a filler to a polymer increases the

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viscosity of the resulting compound when the polymer is melted. Significantly increased viscosity decreases a polymer's moldability. If the addition of filler is over a certain level, the compound may become so 5 viscous that it cannot be injection-molded. In some applications, however, higher filler loading is required to achieve the targeted properties.

The following examples illustrate the product and process of this invention.

10

Example 1:

A fly ash received from the American Electric Power (AEP) was beneficiated using the method described by USP 5,047,145 to produce a clean ash. The 15 beneficiation included gravitationally separating cenospheres from a fly ash slurry; separating a magnetic fraction from the slurry by subjecting the slurry to a magnetic field; and separating the unburned carbon from the slurry by froth flotation. The LOIs of 20 the fly ash before and after beneficiation showed the as-received ash had a carbon content of 23.3%, which was reduced to 1.2% after beneficiation. The concentrations of the components other than carbon increased considerably as a result of the large amount 25 of carbon removed using the beneficiation process. However, due to the removal of magnetic particles during the magnetic separation phase of the process, the  $Fe_2O_3$  content did not increase as much, and changed 30 from 5.29 weight percent prior to beneficiation to 5.32 weight percent in the clean fly ash.

30

35

The clean ash had a mean particle size of about 30 microns distributed in the range from about 0.9 to 176 microns. The clean ash was completely dried to remove all water by placing the clean ash in an oven at 105°C for about 24 hours. The dried ash was then charged into a Majac Model A-12 Acucut air classifier (Hosokawa Micron Powder Systems, Summit, NJ). The operating parameters included a flow rate of 55 standard cubic

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feet per minute (SCFM), a feed rate of 20 pounds per hour (lb/hr), and a rotation speed of 1,000 rotations per minute (RPM). After classifying for approximately 120 minutes, the air classification yielded 16.7%  
5 (over 3 kilograms) of finer spherical particles with a mean particle size of about 4.13 microns, and 83.3% coarser particles with a mean particle size of about 38.3 microns. Table 2 shows the particle size distributions of the finer particle fraction. About  
10 79% fall in the narrow size range of 2.8 to 7.8 microns.

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Table 2  
Particle Size Distribution of Fine Clean Ash

5	Particle size, microns	Cumulative %, passing	Volume %, passing
	22	100.0	0.0
	16	100.0	1.2
	11	98.8	5.9
10	7.8	92.9	15.1
	5.5	77.8	20.9
	3.9	57.0	23.8
	2.8	33.1	19.7
	1.9	13.4	7.5
15	1.4	6.0	4.4
	0.9	1.5	1.5

The most important characteristics for a plastic  
filler are mean particle size, size distribution,  
20 shape, oil absorption, loose density, tap density,  
brightness, pH, and composition. After air  
classification had been used to make a cut at 5 microns  
with the clean ash, the resulting fine fraction was  
characterized according to these properties. The  
25 particle shape associated with the fine fraction of the  
clean ash is shown in Figure 1. The particles are  
primarily spherical except for a few irregularly shaped  
impurities. The particle size distribution has been  
given in Table 2 for ash classified by the set of  
30 operating conditions described in Test No. 10. The  
mean particle size, loose and tap densities,  
brightness, pH, and oil absorption of this fine clean  
ash are presented in Table 3.

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The particle size and size distribution was analyzed using a Leeds & Northrup Microtac analyzer. The particle shape was established using a JEOL JSM 820 scanning electron microscope (SEM). The loose density was measured by charging the ash into a 100 milliliter (ml) graduated cylinder weighing the 100 ml ash, and simply dividing the weight by the 100 ml. The tap density was measured by charging ash into a 100 ml graduated cylinder, taping the cylinder 100 times on a 5 Stave 2003 stamp volumeter, measuring the weight and volume, and again simply dividing the weight by the volume. The oil absorption was determined by following the ASTM standard D281. Brightness was determined using a ZEISS photoelectric reflectance photometer with 10 a swing-in brightness standard at brightness of 95.9% on which a magnesium oxide standard gives a reading of 15 100. The pH was measured following the ASTM standard D4972.

20 Table 3  
Characteristics of Fine Clean Ash as a Plastic Filler

Properties	AEP-C-4M
Mean particle size, microns	4.13
Loose density, g/cc	0.804
25 Tap density, g/cc	0.874
Brightness	24.2
pH	6.6
Oil absorption, lbs/100 lb	30

30 Example 2:

Fly ash was beneficiated, dried and fed into an air classifier as in Example 1, however, the operating parameters of the air classifier were adjusted so the 35 rotational speed was 1800 RPM. This yielded 5.37% fines fraction with a mean particle size of 2.95 microns and 94.6% coarse fraction with a mean particle size of 35.1 microns. Table 4 shows that 88.6% of

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the finer fraction fall in the size range of 1.9 to 5.5 microns.

Table 4  
Particle Size Distribution at 1800 RPM

5	Particle size, microns	Cumulative %, passing	Volume %, passing
	22	100.0	0.0
	16	100.0	0.0
	11	100.0	0.0
10	7.8	100.0	3.7
	5.5	96.3	11.1
	3.9	85.2	35.2
	2.8	50.0	32.1
	1.9	17.9	10.2
15	1.4	7.7	5.8
	0.9	1.9	1.9

Example 3:

20 Fly ash was beneficiated as in Example 1. The clean fly ash was not dried and was charged into a Mozley Model C1009 Ten-Millimeter hydrocyclone (Carpco, Inc., Jacksonville, FL) which was installed with a 3.2 mm vortex finder outlet diameter and a 2.0 mm spigot incorporated in the hydrocyclone body. The hydrocyclone was operated with an inlet pressure of 100 psi and a throughput of 0.25 m<sup>3</sup>/hour. The classification yielded 26.5% fines fraction with particles having a mean size of 7.2 microns (67% of 25 the fines fraction particles fall in the size range of 2.8 to 7.8 microns as shown in Table 5), and 73.5% 30 coarse fraction having a mean particle size of 31.7 microns.

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Table 5  
Particle Size Distribution Using Hydrocyclone

	Particle size, microns	Cumulative %, passing	Volume %, passing
5	88	99.8	1.2
	62	98.5	1.6
	44	97.0	1.5
	31	95.5	0.5
	22	95.0	1.0
10	16	94.0	3.9
	11	90.0	8.3
	7.8	81.8	14.8
	5.5	67.0	18.5
	3.9	48.4	17.8
15	2.8	30.6	15.9
	1.9	14.8	7.7
	1.4	7.1	5.1
	0.9	2.0	2.0

20

COMPARATIVE EXAMPLE 1:

Mineral fillers are widely used in plastic products to improve performance and reduce the costs.

The minerals commonly used for plastic fillers

25 include calcium carbonate, kaolin, aluminum trihydrate, talc and titanium dioxide, however, calcium carbonate accounts for about 70% of the fillers used. Table 6 shows the characterization of a commercial carbonate filler, Gama-Sperse CS-11,

30 which was precoated with 1% stearate, and a commercial alumino-silicate filler. Table 7 gives the particle size distribution information of the

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commercial fillers. Figure 2 shows the commercial alumino-silicate filler's shape. In comparison with the commercial fillers, the fly ash filler (Table 3) has similar mean particle size, narrower size 5 distribution, a reduced variation in the loose and tap densities, and similar oil absorption to that of alumino-silicate filler. The pH of the fly ash filler also falls between the two commercial fillers. The major differences are the lower brightness and 10 spherical shape of the fly ash filler. While the lower brightness of the ash may slightly reduce the potential spectrum of applications, the spherical shape of the ash particle could improve the structural characteristics of polymers compounded 15 with ash resulting in a very broad spectrum of industrial or other applications where brightness is not an important factor.

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Table 6

Characteristics of Commercial Calcium Carbonate  
and Alumino-Silicate Fillers

	Properties	Calcium	Alumino-silicate
		carbonate filler	filler
5	Gama-Sperse CS-		ASP 400P
	11		
5	Mean particle size, microns	3.0	4.8
	Loose density, g/cc	0.56	0.38
10	Tap density, g/cc	n/a	0.72
	Brightness	94	79-82
	pH	9.5	3.5-5.0
	Oil absorption, lbs/100 lb.	16	30-35

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Table 7

## Particle Size Distribution of Calcium Carbonate and Alumino-Silicate Fillers

5	Particle Size	Bottom Sample		Top Sample	
		Microns	Cum., %	Volume, %	Cum., %
	22		100.0	0.0	100.0
	16		100.0	4.5	94
10	11		95.5	9.5	87
	7.8		86.0	13.5	77
	5.5		72.5	15.0	56
	3.9		57.5	17.5	42
	2.8		40.0	12.0	30
15	1.9		28.0	6.0	20
	1.4		22.0	7.5	14
	0.9		14.5	14.5	7
					7

20 Example 4: Comparison of plastics filled with fly ash vs. commercial filler:

25 Three polymers (polypropylene, low density polyethylene, and high density polyethylene) were compounded with a fine fraction of the clean ash as obtained in Example 1. Specifically, polypropylene homopolymer T-3922 nat, Escorene LL 6407.67 nat. linear low density polyethylene, and HXM 50100 nat. high density polyethylene, produced by Fina Oil & Chemical Company, Exxon Chemical Americas, and 30 Phillips Petroleum, respectively. For comparison, a

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commercial CaCO<sub>3</sub> filler was compounded with the same three polymers under the same conditions.

The resulting three compounds were used to produce two different automotive parts, a trim clip and a component to support an under the hood wiring harness. The trim clip was chosen as a result of the symmetrical and cavity layout and because the major surfaces were parallel and perpendicular to the runner. In addition, the wiring harness contained large radii and smooth surfaces that would provide a good indication of the surface quality that could be expected from compounds containing fly ash.

The fine ash from Example 1 was coated with silane using the following procedure: Dow Corning Z-6032 Silane in an amount of 0.5 weight percent based on the weight of the fly ash was diluted by adding 100 times by weight distilled water. The silane solution was mixed with ash for about 10 minutes and placed in an oven to dry. After all of the water evaporated, the coated ash powder was then crushed through a 100 mesh screen.

Each of the three polymers individually were compounded with the coated ash powder and compounded with calcium carbonate at concentrations of 10, 20, 25 40 and 80 parts per hundred parts of resin by weight (phr). Each of the polymer/filler batches were mixed for 30 minutes in a Brabender Plasti-Corder torque-rheometer at 50 RPM. The mixing temperatures were 250 C, 190 C and 200 C for polypropylene, low density 30 polyethylene, and high density polyethylene, respectively.

An Arburg 221-75-350 injection molding machine with a four-cavity standard tensile specimen mold was used to form the test specimens. This machine is capable of providing 35 tons of clamping force and 35 7.5 tons of injection force. The multi-cavity mold was jacketed with water to regulate the temperature of the mold. The water temperature was in turn

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controlled by a Model TDW-1NX conditioner, manufactured by Application Engineering Corporation. The mold was maintained at a temperature of about 100°F. If a polymer and filler mixture proved to be 5 injection moldable, ten tensile specimens were produced from each batch for mechanical testing.

The compounds produced were granulated down to a size that would flow freely from a feed hopper through the feed chute and into the barrel of a 10 commercial injection molding machine. Most of the granules were approximately 3 to 6 millimeters in diameter.

The modules of elasticity, elongation, yield and ultimate strengths of the specimens produced by 15 injection molding were determined using an Instron testing system following the ASTM standard D638 method. If the elongation of a specimen was less than 40%, the elongation was measured by an extensometer automatically. If the elongation of a 20 specimen was greater than 40%, the elongation was measured manually.

Observations were made with the assistance of a scanning electron microscope (SEM) on the fracture surfaces of the broken tensile specimens to examine 25 the bonding between the polymers and the fillers.

The compounds discussed above were injection-molded at a temperature and pressure intentionally lower than conventional for injection molding. The temperature and pressure is not critical and suitable 30 ranges can be readily determined by one of skill in the art taking into consideration the type of plastic being molded, the filler being used and the amount of filler. If the polymer compounds could not be injected, the injection pressure was gradually increased until the compound could be injected fully 35 into the mold. If the maximum pressure could not inject the compound, the mold temperature was increased gradually without surpassing the upper

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limit of the suggested injection temperature for the polymer. Tables 8, 9 and 10 list the injection molding parameters for the polypropylene, low density polyethylene, and high density polyethylene compounds 5 as well as the various concentrations of fine AEP ash and the commercial calcium carbonate fillers used.

A VanDorn, Model #75-RS-4F, injection machine was used to process the ash filled compounds. Upon injection of the trim clip the material flowed well, 10 cavities were filled uniformly, lines were well-defined, and parting of the product was realized without the addition of a mold release. Operation of the machine using the experimental fly ash compounds could not be distinguished from operation of the 15 machine using the commercial materials typically used to produce the trim clips. The injection of the wiring harness support proceeded satisfactorily. Though the shape was of a nature that considerably more resistance would be encountered, the material 20 readily filled the cavities. Adjustments were made to the injection pressure, holding pressure and back pressure yet the new settings were typical given the nature of the die and not a result of the variation in the compound being injected.

25 Filler levels, using either AEP ash or calcium carbonate, at or below 80 phr in polypropylene did not result in any difficulties in the injection molding of the compounds. Each were injection-molded under the conditions listed in Table 8.

30 The addition of fillers in the low density polyethylene decreased the moldability of the compound more significantly. The injection pressure had to be increased to overcome the increase in viscosity as the filler content increased. The low 35 density polyethylene with 40 phr fly ash required 700 psi injection pressure, while the same polymer with 40 phr calcium carbonate filler required 900 psi pressure, as shown in Table 9. When the loading

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level increased to 80 phr, the low density polyethylene with fly ash was still moldable but the same polymer with calcium carbonate filler was not, even though the injection pressure had been increased 5 to the maximum 2200 psi.

The high density polyethylene proved more difficult to inject because of its higher viscosity. The injection pressure had to be greater than 1200 psi in order to fully fill the mold cavity even for 10 the pure polymer. The addition of fly ash filler in the levels below or equal to 40 phr did not cause any injection problems, but the addition of calcium carbonate filler in the amount of 40 phr introduced a significant increase in viscosity. The injection 15 pressure had to be adjusted to a maximum of 2200 psi, the mold temperature was raised from 100F to 140F, and the injection temperature had to be increased to the highest suggested temperatures for this polymer, but this compound still could not be injected into 20 the cavity fully.

These injection molding tests indicate that polypropylene, and low and high density polyethylenes compounded with fine AEP ash have similar or better moldability than the same polymers when compounded 25 with a commercial calcium carbonate filler.

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Table 8

## Injection Molding Test of Polypropylene with Fillers

Filler	Filler Content phr	Zone I	Zone II	Zone	Zone	Inject.	Inject.	Hold.	Mold
		Temp. °C	Temp. °C	III Temp. °C	IV Temp. °C	Veloc. Dial*	Press. psi	Press. psi	Temp. °F
None	0	210	220	210	200	5.0	400	100	100
Fly Ash	10	210	220	210	200	5.0	400	100	100
CaCO <sub>3</sub>	10	210	220	210	200	5.0	400	100	100
Fly Ash	20	210	220	210	200	5.0	400	100	100
CaCO <sub>3</sub>	20	210	220	210	200	5.0	400	100	100
Fly Ash	40	210	220	210	200	5.0	400	100	100
CaCO <sub>3</sub>	40	210	220	210	200	5.0	400	100	100
Fly Ash	80	210	220	210	200	5.0	400	100	100
CaCO <sub>3</sub>	80	210	220	210	200	5.0	400	100	100

\*Dial 5.0 is the maximum injection velocity of the machine.

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Table 9

## Injection Molding Test of Low Density Polyethylene with Fillers

Fillers	Filler	Zone I	Zone II	Zone III	Zone IV	Injection	Injection	Holding	Mold
	Content	Temp.	Temp.	Temp.	Temp.	Velocity	Pressure	Pressure	Temp.
	phr	°C	°C	°C	°C	Dial	psi	psi	°F
None	0	210	220	210	200	5.0	500	100	100
Fly Ash	10	210	220	210	200	5.0	500	100	100
CaCO <sub>3</sub>	10	210	220	210	200	5.0	500	100	100
Fly Ash	20	210	230	220	210	5.0	700	100	100
CaCO <sub>3</sub>	20	210	230	220	210	5.0	700	100	100
Fly Ash	40	220	230	220	210	5.0	700	100	100
CaCO <sub>3</sub>	40	220	230	220	210	5.0	900	100	100
Fly Ash	80	220	230	220	210	5.0	900	150	100
CaCO <sub>3</sub> *	80	240	250	240	230	5.0	2200	150	120

\*This material could not be injected even at the maximum pressure 2200 psi.

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Table 10

## Injection Molding Test of High Density Polyethylene with Fillers

Fillers	Filler Content phr	Zone I	Zone II	Zone III	Zone IV	Injection Velocity Dial	Injection Pressure psi	Holding Pressure psi	Mold Temp. °F
		Temp. °C	Temp. °C	Temp. °C	Temp. °C				
None	0	260	260	250	250	5.0	1200	100	100
Fly Ash	10	260	260	250	250	5.0	1200	100	100
CaCO <sub>3</sub>	10	260	260	250	250	5.0	1200	100	100
Fly Ash	20	260	260	250	250	5.0	1200	100	100
CaCO <sub>3</sub>	20	260	260	250	250	5.0	1200	100	100
Fly Ash	40	260	260	250	250	5.0	1200	100	100
CaCO <sub>3</sub> *	40	290	290	270	270	5.0	2200	100	140

\*This material could not be injected even at the maximum pressure 2200 psi.

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Turning now to mechanical properties, the ultimate tensile strength, yield strength, elongation and Young's modules are the most important mechanical properties for polymer materials. Filler content, 5 filler particle size, size distribution, shape, mixing quality, and bonding between filler and polymer matrix all affect the mechanical properties. As a rule, higher filler content leads to higher yield strength and an increase in the Young's modules while a lower 10 elongation would be expected because the filler particles restrict deformation of the polymers. The fillers also affect the ultimate tensile strength (UTS) in two ways. First, the filler particles cause stress concentration and imitate cracks, decreasing UTS. 15 Second, if the particles have the proper shape and strong bonding between the particles and the polymer matrix, the particles may serve to reinforce the polymer, resulting in higher UTS. With regard to size, larger particles usually reduce the UTS and elongation. 20

The UTS of the article is preferably greater than about 500 pounds per square inch (psi), more preferably greater than about 2000 psi.

Table 11 represents the mechanical properties of polypropylene with fly ash and calcium carbonate 25 fillers. This table indicates that the yield strength and Young's modules increases and UTS and elongation decreases as the filler content increases, except when calcium carbonate content is over 40 phr. At this level the calcium carbonate filler begins to decrease 30 the yield strength as well as the Young's modules. With lower calcium carbonate contents of 10 and 20 phr, the polypropylene compound shows higher UTS than those of the polymers with fly ash filler. When the calcium carbonate content exceeds 40 phr, the UTS of the 35 compound is lower than that of the compounds with ash as the filler. The yield strength and Young's modules of the polypropylene with an ash filler are higher than those of polypropylene with calcium carbonate filler,

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but the elongation is lower than that of the counterpart. In general, ash filler can replace calcium carbonate filler to reach the equivalent mechanical properties when the filler content is less than or equal to about 20 phr.

5 Table 12 shows the results of the mechanical tests for the low density polyethylene with ash and calcium carbonate fillers. The low density polyethylene with ash filler have better mechanical properties than those of the same polymer with calcium carbonate filler. This superiority is more obvious at the higher loading level of 40 phr.

10 15 Table 13 gives the mechanical properties for the high density polyethylene with ash and calcium carbonate fillers. The noticeable phenomenon is that the UTS increases when filler content reaches 40 phr for the polymer with ash filler. This indicates that the ash filler may reinforce the polymer matrix.

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Table 11

## Mechanical Properties of Polypropylene with Fillers

5	Filler	Filler	Ultimate	Yield	Elongation	Young's
		Content	Tensile	Strength	%	Modules,
		phr	Strength, psi	psi		ksi
10	None	0	6666	1728	650	185
	Flyash	10	4724	2199	630	189
	CaCO <sub>3</sub>	10	5024	1880	650	164
15	Flyash	20	4378	2340	467	211
	CaCO <sub>3</sub>	20	4928	2114	600	178
	Flyash	40	4267	2416	32	237
	CaCO <sub>3</sub>	40	3850	1738	367	125
15	Flyash	80	3953	2474	1.3	314
	CaCO <sub>3</sub>	80	2900	1480	41.7	217

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Table 12

## Mechanical Properties of Low Density Polyethylene with Fillers

		Filler Content	Ultimate Tensile Strength, psi	Yield Strength psi	Elongation %	Young's Modules, ksi
5	Filler	phr				
	None	0	3336	485	467	27.5
	Flyash	10	3463	557	467	36.0
10	CaCO <sub>3</sub>	10	3255	545	467	33.4
	Flyash	20	2635	560	462	39.4
	CaCO <sub>3</sub>	20	2563	573	483	33.6
	Flyash	40	2449	738	450	47.3
15	CaCO <sub>3</sub>	40	1905	574	442	33.6
	Flyash	80	2377	888	46.6	90.5
	CaCO <sub>3</sub>	80	--	--	--	--

-30-

Table 13

## Mechanical Properties of High Density Polyethylene with Fillers

5	Filler	Filler Content	Ultimate Tensile Strength, psi	Yield Strength, psi	Elongation %	Young's Modules, ksi
	Filler	phr				
	None	0	5040	1016	60	79.4
	Flyash	10	4843	1192	45	73.2
	CaCO <sub>3</sub>	10	3807	940	83	45.2
10	Flyash	20	4823	1160	50	81.6
	CaCO <sub>3</sub>	20	3698	1089	84	56.6
	Flyash	40	5219	1279	28	96.4
	CaCO <sub>3</sub>	40	--	--	--	--

15 In general, the polypropylene and high density polyethylene with fine clean ash filler show equivalent or better strengths and Young's modules, but the elongation is not as good as those of the same polymers with the commercial carbonate filler, Gama-Sperse CS-20. The low density polyethylene with the fine clean ash filler shows superiority over the same polymer with calcium carbonate filler in all measured mechanical properties at various loading levels.

25 SEM images indicate generally the fillers were homogeneously mixed with the polymers. Figures 3 to 8 show the fracture surfaces of the polypropylene, low density polyethylene and high density polyethylene with 40 phr ash filler and 40 phr calcium carbonate filler. Good bonding between the ash filler and the three 30 polymers can be seen in Figures 3, 5, and 7. Figures 4, 6 and 8 give examples of calcium carbonate filler and polymer bonding. It appears that fly ash, along with the silane coupling agent, has better bonding with the three polymers than the calcium carbonate does.

35 With respect to the surface finish, those materials containing 10 phr displayed very smooth,

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s somewhat glossy surfaces. Injection of those compounds containing 20 phr produced parts that had a somewhat opaque finish, and a very smooth surface. The parts made from materials containing 40 phr displayed an uneven surface that was dull in nature and revealed flow patterns in many cases. This was not uncommon with compounds containing a considerable amount of filler which displayed the same characteristics with regard to the surface quality.

Overall, the resulting products indicated that a quality finish may be achieved when using these ash filled materials in the injection molding of commercial products.

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What is claimed is:

1. A process for producing a filler from a fly ash material, the process comprising the steps of:
  - 5 a) cleaning the fly ash material to remove at least a portion of the carbon, cenosphere or magnetic content; and
  - b) size classification of the fly ash material to obtain a fines fraction having a mean particle size 10 less than about 30 microns.
2. The process of claim 1 wherein the mean particle size of the fines fraction is less than about 20 microns.
- 15 3. The process of claim 1 wherein the mean particle size of the fines fraction is less than about 10 microns.
- 20 4. The process of claim 1 wherein the size classification step comprises air classification or wet classification.
- 25 5. The process of claim 4 wherein the size classification step comprises air classification at a rotation speed of about 1000 to about 2000 rotations per minute.
- 30 6. The process of claim 1 wherein the cleaning step comprises froth flotation, burning, electrostatic separation, gravitational separation or magnetic separation.
- 35 7. The process of claim 1 wherein the cleaning step comprises froth flotation.

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8. The process of claim 1 wherein the cleaned fly ash material has a residual carbon content of less than about 6%.

5 9. The process of claim 1 wherein the cleaned fly ash material has a residual carbon content of less than about 3%.

10 10. The process of claim 1 wherein the cleaning step is performed after the size classification step.

11. The process of claim 1 wherein the filler is used in a plastic article or in a paint or in other coatings.

15 12. A process for producing a filler from a fly ash material, the process comprising the steps of:  
a) cleaning the fly ash material to remove at least a portion of the carbon content; and  
20 b) size classification of the fly ash material to obtain a fines fraction having a mean particle size less than about 30 microns.

25 13. A process for the manufacture of a plastic article comprising the steps of:  
a) cleaning a fly ash material to remove at least a portion of the carbon, cenosphere or magnetic content;  
30 b) size classification of the fly ash material to obtain a fines fraction having a mean particle size less than about 30 microns; and  
c) compounding the clean fines fraction with a plastic matrix to form a compound.

35 14. The process of claim 13 further comprising the step of calcining the fly ash material to remove surface contamination.

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15. The process of claim 13 further comprising the step of coating the fly ash material with a coupling agent to improve bonding between the fly ash material and the plastic matrix.

5

16. The process of claim 13 wherein the fines fraction has a mean particle size less than about 20 microns.

10

17. The process of claim 13 wherein the plastic matrix includes a thermosetting plastic, a thermoplastic, an advanced thermoplastic or an automotive elastomer.

15

18. The process of claim 13 wherein the plastic matrix includes polyethylene, polypropylene, polyvinyl chloride (PVC), polystyrenes, polyacrylics, polycarbonate, acrylonitrile-butadiene-styrene resin (ABS), polyethylene terephthalate (PET), nylon, phenolic resins, polymethyl methacrylate, polyamides, polyester, polyurethane, or thermoplastic polyolefin (TPO).

20  
25  
19. The process of claim 13 wherein the plastic matrix comprises a polyethylene or a polypropylene.

20. The process of claim 13 wherein the cleaning step is performed after the size classification step.

30

21. The process of claim 13 wherein the cleaning step comprises froth flotation to remove at least a portion of the carbon content.

35

22. The process of claim 13 wherein the cleaning step comprises froth flotation, burning, electrostatic separation, gravitational separation or magnetic separation.

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23. The process of claim 13 wherein the compounding step comprises mixing the clean fines fraction with the plastic matrix, and heating the mixture.

5

24. The process of claim 23 wherein the plastic matrix is in a solid pellet form, a powder form, a liquid form, or a semi-liquid form during mixing with the clean fines fraction.

10

25. The process of claim 13 further comprising the step of injection molding, extrusion molding or compression molding the compound.

15

26. The process of claim 13 wherein the concentration of clean fines fraction is less than about 500 parts per hundred parts of plastic matrix by weight.

20

27. A process for the manufacture of a plastic article comprising the steps of:

- a) cleaning a fly ash material to a carbon content less than about 6%;
- b) size classifying the fly ash material to obtain a fines fraction having a mean particle size less than about 10 microns;
- c) mixing the clean fines fraction with a plastic matrix to form the mixture, the plastic matrix comprising polyethylene, polypropylene, PVC, polycarbonate, ABS or nylon; and
- d) heating the mixture to form a compound.

28. The process of claim 27 wherein the plastic matrix comprises polyethylene or polypropylene.

35

29. The process of claim 27 further comprising the step of injection molding the compound.

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30. A process for producing a filler from a fly ash material, the process comprising the steps of:

5 a) cleaning the fly ash material to remove at least a portion of the carbon, cenospheres or magnetic particles; and

b) grinding the fly ash material to a mean particle size less than about 30 microns.

31. A plastic article comprising:

10 a) a plastic matrix; and

b) a fly ash filler having a mean particle size of less than about 30 microns.

15 32. The plastic article of claim 31 wherein the fly ash filler has a mean particle size less than about 10 microns.

20 33. The plastic article of claim 31 wherein the article has an ultimate tensile strength of at least about 2000 psi.

25 34. The plastic article of claim 31 wherein the article has an ultimate tensile strength of at least about 500 psi.

30 35. The plastic article of claim 31 wherein the plastic matrix comprises polyethylene, polypropylene, polyvinyl chloride (PVC), polystyrenes, polyacrylics, polycarbonate, acrylonitrile-butadiene-styrene resin (ABS), polyethylene terephthalate (PET), nylon, phenolic resins, polymethyl methacrylate, polyamides, polyester, polyurethane, or thermoplastic polyolefin (TPO).

35 36. The plastic article of claim 31 wherein the plastic matrix comprises a thermosetting plastic, a thermoplastic, an advanced thermoplastic, or an automotive elastomer.

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37. The plastic article of claim 31 wherein the plastic matrix comprises high density polyethylene or low density polyethylene.

5 38. The plastic article of claim 31 wherein the fly ash filler is obtained by the process of:

a) cleaning the fly ash material to remove at least a portion of the carbon content, cenospheres or magnetic particles; and

10 b) size classification of the fly ash material to obtain a fines fraction having a mean particle size less than about 30 microns.

15 39. The plastic article of claim 38 wherein the fly ash filler is obtained by the process which further comprises calcining the fly ash material.

20 40. The plastic article of claim 38 wherein the fly ash filler is obtained by the process which further comprises coating the fly ash material with a coupling agent.

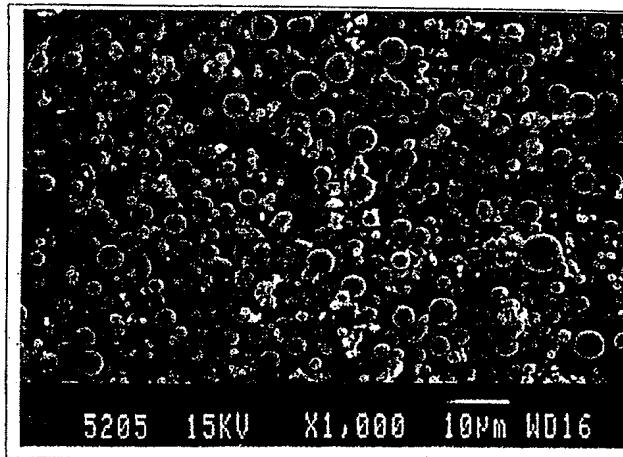


Figure 1. Particle shape of fine clean AEP ash



Figure 2. Particle shape of commercial alumino-silicate filler

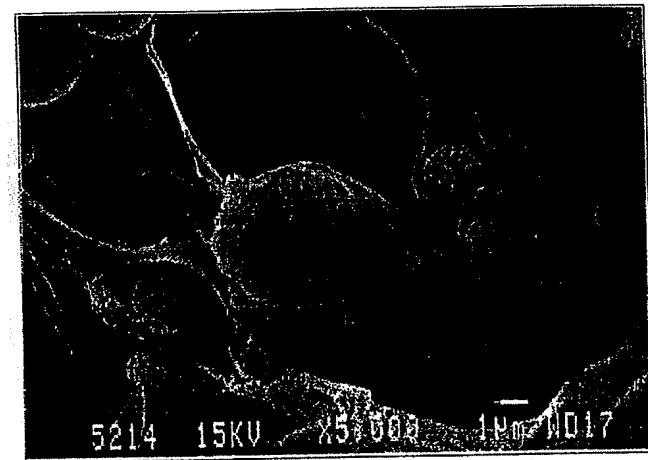


Figure 3 Fracture surface of polypropylene with 40 phr fine clean AEP ash

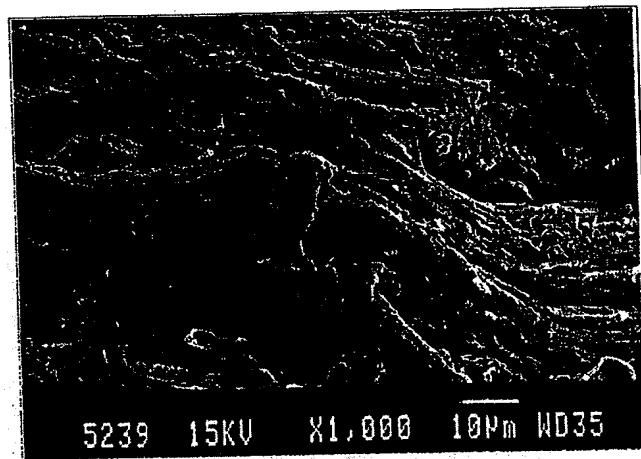


Figure 4 Fracture surface of polypropylene with 40 phr CaCO<sub>3</sub> filler

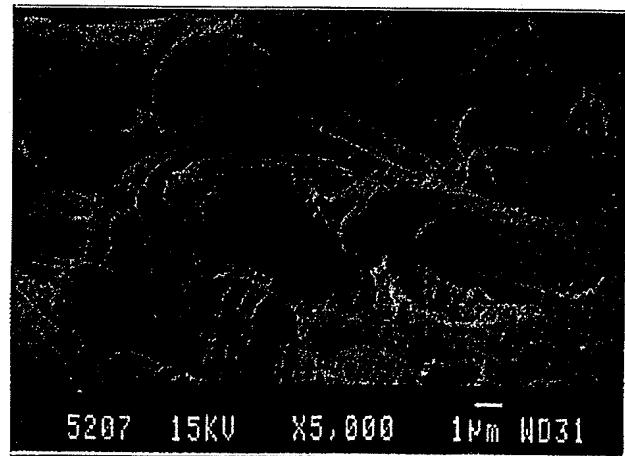


Figure 5 Fracture surface of low density polyethylene with 40 phr fine clean AEP ash

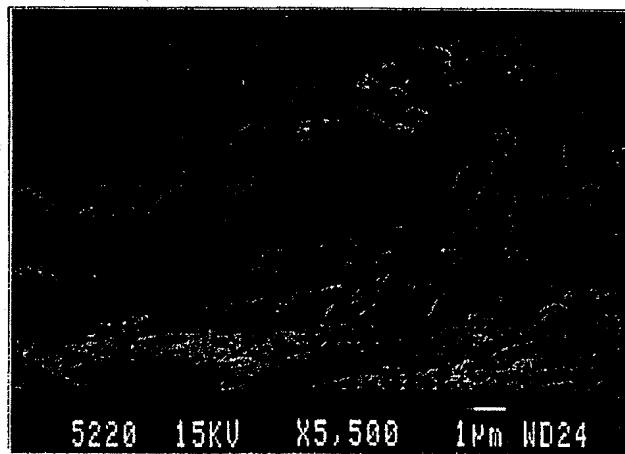


Figure 6 Fracture surface of low density polyethylene with 40 phr CaCO<sub>3</sub> filler

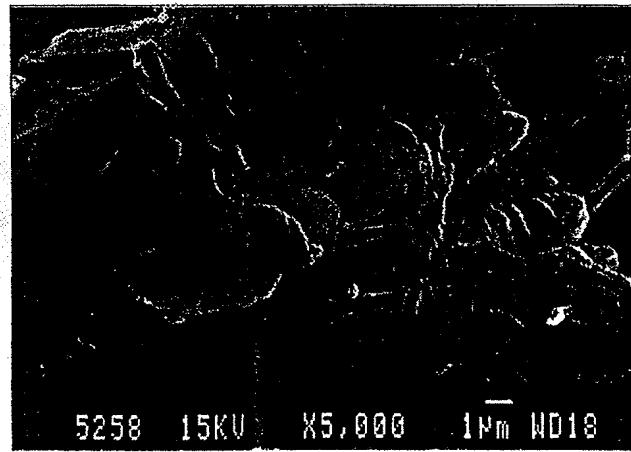


Figure 7. Fracture surface of high density polyethylene with 40 phr fine clean AEP ash

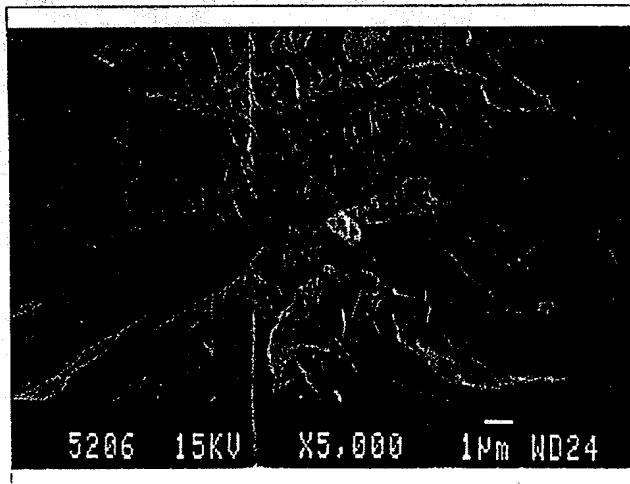


Figure 8. Fracture surface of high density polyethylene with 40 phr CaCO<sub>3</sub> filler

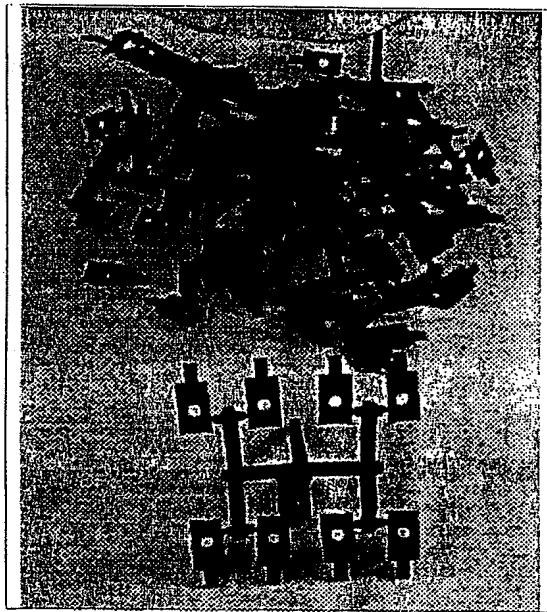


Figure 9. Trim clips produced from one of the ash filled polymers

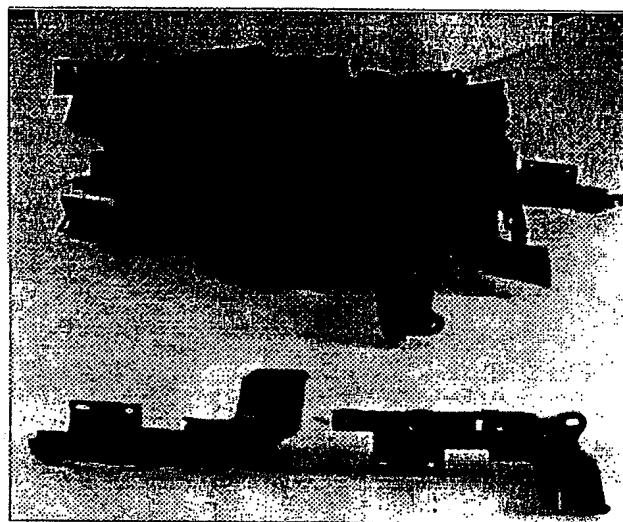


Figure 10. GM wiring harness support produced from one of the ash filled polymers

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/01545

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C04B 14/00  
 US CL :106/400, 401, 405, Dig. 1; 264/Dig. 49

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/400, 401, 405, Dig. 1; 264/Dig. 49

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,227,047 A (HWANG) 13 July 1993, abstract, column 5, line 40-47, claim 7.	1-40
Y	US 4,147,687 A (O'DONNELL) 03 April 1979, abstract.	13-40
Y,A	US 4,229,329 A (BENNETT) 21 October 1980, abstract.	11
Y	US 4,352,856 A (SMILLIE) 05 October 1982, column 2, lines 52 - column 3, line 10.	17-18, 23-24, 35
X	US 4,294,750 A (KLINGAMAN et al.) 13 October 1981, abstract, figures 1 and 3, column 5, line 40, column 8, lines 3-5, 32-35, 48-49, column 10, lines 34-46, 64, claim 1.	1-6, 8-9, 11-20, 22-32, 35-40

 Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 APRIL 1999

Date of mailing of the international search report

26 APR 1999

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/01545

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,047,145 A (HWANG) 10 September 1991, abstract.	1-40